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The Application of Phase Equilibrium Studies on the System CaO-Al_2O_3-SiO_2-Fe_2O_3 to Cement Technology.*

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AN investigation has recently been completed of the phase equilibrium relations in that part of the system of the four oxides, lime, alumina, silica, ferric oxide, which bears on the problem of the constitution of Portland cement. These phase equilibrium relations have been described in a paper[1] recently published, while a detailed analysis of their application to Portland cement is in course of publication.[2] It is the purpose of this paper to present a survey of some of the results obtained, without, however, reproducing the original data on which they are based or describing in detail the methods by which they are derived. For a complete discussion reference should be made to the papers referred to above.

The study of the constitution of Portland cement, that is of the various compounds it contains and the conditions which govern their formation, has been the subject of investigation since the pioneer work of Le Chatelier in 1882. The attention paid in recent years to the development of Portland cements of special properties has caused increased emphasis to be laid on the necessity for accurate knowledge of the constitution of cements. Thus, in order to obtain information that may serve as a useful guide to the cement manufacturer and user, many attempts are now being made to relate quantitatively various properties of cements, such as strength, heat of hydration, shrinkage, and resistance to chemical attack, to the composition of the material. The interpretation of such data and its arrangement in systematic order requires as a

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basis a knowledge of the nature and amount of the various compounds present in any cement. It is therefore necessary to know how the amounts of the various compounds present vary with the composition and conditions of production of the material.

Present knowledge of the constitution of cement is based mainly on the results of studies on phase equilibria in systems containing as their components the more important of the oxides of which Portland cement is composed. Phase equilibrium studies show what compounds are produced at equilibrium in the system under examination, the composition of the mixes from which they will be formed, the melting temperatures, and the compositions of the molten liquids in equilibrium with which the various solid compounds can exist. It is therefore possible, given the necessary data, to define exactly the condition of any mix at any definite temperature provided the mix is known to have reached equilibrium. It is also possible from such data to predict how the mix will differ should equilibrium not be fully attained.

The three oxides, lime, alumina, silica, make up about 90 per cent. of the composition of Portland cement and form the basic system that has to be considered. The paper of Rankin and Wright[3] on the ternary system CaO-Al_2O_3-SiO_2 which was published in 1915 has formed the basis for most subsequent investigations. It was shown from this work that in the region of Portland cement compositions the compounds present in a clinkered mix of the three oxides were $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$, and that free CaO and the compound $5CaO.3Al_2O_3$ might also appear. Later work on the system[4] CaO-SiO_2-Fe_2O_3 showed that in the region of Portland cement compositions the same silicate compounds were formed. Investigation of the system[5] CaO-Al_2O_3-Fe_2O_3 showed the presence of the same calcium aluminate compounds, but that a new alumina-containing compound $4CaO.Al_2O_3.Fe_2O_3$ was formed in addition. From the composition of the mixes from which it was formed it was evident that this compound was to be anticipated in Portland cement.

The applicability of these investigations to the problem of Portland cement constitution was not accepted by all authorities. It was first argued that the equilibrium relations in the ternary systems did not afford sufficient information as to the behaviour of quaternary mixes of the four oxides CaO, Al_2O_3, SiO_2, Fe_2O_3, or of technical Portland cements containing in addition small amounts of magnesia and alkalis. The results of the present work on the quaternary system have provided the required confirmation of the conclusions drawn from the ternary system in regard to the nature of the compounds formed. It was further objected that Portland cement clinker did not attain equilibrium on clinkering under the practical conditions of cement manufacture, and that conclusions drawn from studies on systems in equilibrium could not therefore be applied to it. Investigations of the optical properties and X-ray diffraction patterns of Portland cement clinkers,[6] and of the composition of certain almost pure crystalline components separated by centrifugal methods from crushed clinker,[7] combined with the information yielded by the determination by the

modern analytical methods of the free lime contents of cements have, however, now provided evidence that may be regarded as conclusive as to the presence in Portland cements of the compounds predicted by the phase equilibrium studies. The cumulative result of all the evidence is to show that Portland cement clinker approaches closely to equilibrium at the clinkering temperature, and differs from it only in that a small amount of lime may remain uncombined ; this merely reduces the content of the tribasic compounds in a manner which is easily calculated.

Bogue[8] has applied the conclusions drawn from the earlier phase equilibrium work on ternary systems to the approximate calculation of the amounts of the compounds present in Portland cement. The method is briefly as follows. The gross analytical composition of the cement is taken and from the total lime content is subtracted the lime present as free lime and calcium sulphate. The remaining lime, together with the ferric oxide, alumina, and silica, are calculated to the compounds $4CaO.Al_2O_3.Fe_2O_3$, $3CaO.Al_2O_3$, $2CaO.SiO_2$ and $3CaO.SiO_2$. This calculation assumes that the cement clinker is in complete equilibrium, apart from the correction applied for the free lime. It therefore assumes not only that the clinker reaches equilibrium at the clinkering temperature, but that equilibrium is also maintained during cooling. This latter assumption will be seen later to be the source of errors which may be considerable. The magnesia and alkalis present in the cement are ignored in this calculation, but since the amount of the alkalis is always small, and there is evidence that part at least of the magnesia is present in an uncombined condition[9], the errors from this source are not likely to be appreciable.

Before considering the quaternary system $CaO-Al_2O_3-SiO_2-Fe_2O_3$ it will be convenient to discuss certain applications of the earlier work on ternary systems in order to appreciate in full the nature of the problems which have been brought much nearer to complete solution by the work on the quaternary system.

NOMENCLATURE.—It is customary and convenient when dealing with the molecular compounds with which we shall be concerned to use abbreviated formulæ as a form of shorthand notation as follows: $C_3S = 3CaO.SiO_2$; $C_2S = 2CaO.SiO_2$; $C_3A = 3CaO.Al_2O_3$; $C_5A_3 = 5CaO.3Al_2O_3$; $C_4AF = 4CaO.Al_2O_3.Fe_2O_3$.

The Ternary System—$CaO-Al_2O_3-SiO_2$.

The phase equilibrium diagram for the system $CaO-Al_2O_3-SiO_2$ is shown in Fig. 1, which is plotted somewhat differently from the usual and more familiar type used when aqueous three component systems are under consideration. The usual type of diagram for aqueous ternary systems is an isothermal one, that is, it shows the solubility curves at one temperature only. Fig. 1 is a polythermal diagram ; it does not show solubility curves, but a series of fields, known as primary phase fields, from each of which one compound is the first solid to separate when a completely melted mix of a composition falling within the field is allowed to cool. For example, the area KED is the primary phase

field for tricalcium silicate, the area MKEHIPQR for dicalcium silicate, and the area BDEHG for tricalcium aluminate. The temperatures at which solid first separates are not constant over such fields, and the variation of these temperatures may be shown by inserting isotherms on the diagram. This is not done in Fig. 1 in order to avoid complexity, but is done in Fig. 2. The boundary between two fields is a line along which two solids separate and exist together in contact with the liquid. The point where three primary phase fields meet represents the liquid composition and temperature at which three solids can exist together

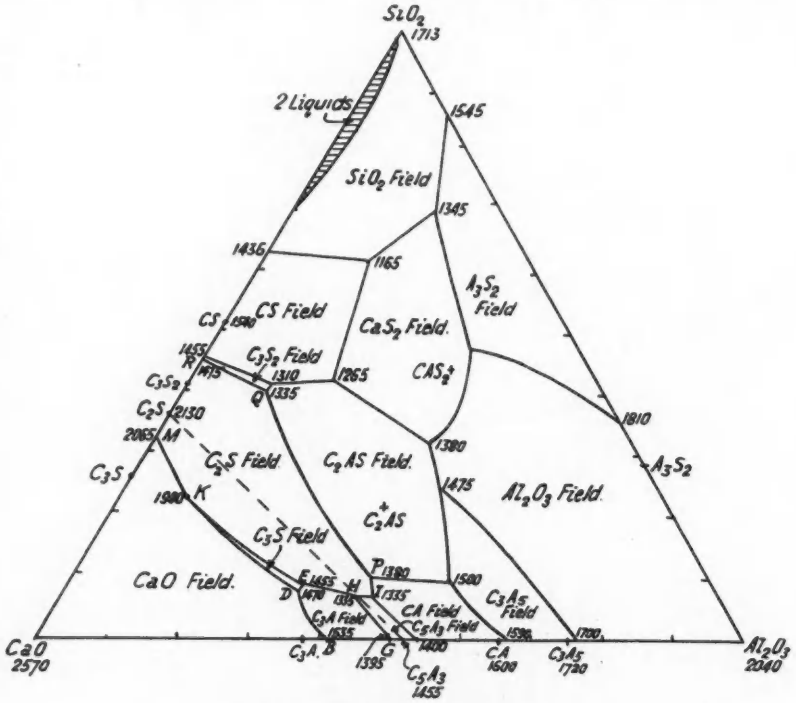

Fig. 1.—System CaO–Al_2O_3–SiO_2.

in equilibrium with liquid. In accordance with the requirements of the phase rule for a condensed system of three components, the equilibrium of three solids and liquid can only exist for one single condition of temperature and liquid composition.

The crystallisation path of any mix from the completely melted condition may take a number of different forms. In the simplest case the solid corresponding to the primary phase field in which the mix composition lies will separate first, and, as it separates, the liquid composition will move across the field along

the line obtained by joining the composition of the separating solid and the original mix composition and producing it. As the temperature falls the liquid composition moves along this line until it intersects a boundary curve. Here a second solid commences to separate and the liquid composition moves down the boundary curve in a direction of falling temperature until an invariant point or eutectic is reached. The mix finally becomes completely solid at this point. As an example a mix of composition (iii), Fig. 2, is completely liquid at about 1,700 deg. C. On cooling it first separates solid C_3S and the liquid moves

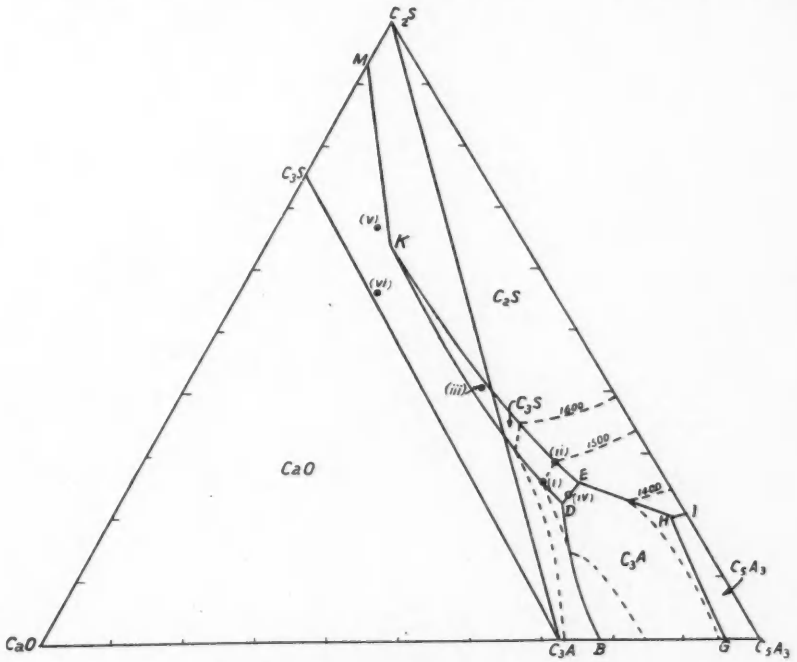

Fig. 2.—System CaO–$2CaO.SiO_2$–$5CaO.5Al_2O_3$.

along the line C_3S—(iii) produced until it intersects the boundary curve DE at (iv). Here C_3A commences to separate also, and the liquid composition moves along DE towards E. When E is reached C_2S separates in addition, and the mix goes entirely solid at this point.

Many crystallisation paths are not so simple as this, as will be seen later, and solids which first crystallise out from a liquid mix may completely redissolve again and disappear before final solidification of the whole mix occurs.

The region of compositions with which we are concerned in studying the equilibria of Portland cement is only a small part of the whole ternary system

CaO-Al_2O_3-SiO_2 and lies within a smaller ternary system made up by taking as components CaO, $2CaO.SiO_2$, and $5CaO.3Al_2O_3$. This system, which is divided from the main system in Fig. 1 by the dotted line running from C_2S to C_5A_3, is shown enlarged as a separate ternary system in Fig. 2.

Equilibrium between Clinker and Liquid in Ternary Systems.

In the manufacture of Portland cement a raw mix is heated to a temperature at which clinkering occurs ; at this temperature a portion of the mix, amounting to 20 to 30 per cent., becomes liquid while the remainder is still in the solid state. The equilibrium which exists between the liquid and solid phases at the clinkering temperature is of fundamental importance to our knowledge of cement constitution. We may first consider these equilibrium relations in ternary systems before attempting to deal with the quaternary system.

The region of Portland cement compositions, expressed only in terms of lime, alumina, and silica, lies in a region around the point K in Fig. 2. When a mix of a composition falling in this region is heated to a clinkering temperature of say 1500 deg. C. the solid, when equilibrium is established, may consist of C_3S, C_2S and C_3S, or CaO and C_3S. The liquid compositions lie on that portion of the 1500 deg. C. contour line which falls between the two boundaries of the C_3S field, that is between (i) and (ii) in Fig. 2. It is seen that while original mix compositions around the point K fall into the triangle C_3S-C_3A-C_2S, the liquids which are formed lie on the low lime side of this triangle in the triangle C_2S-C_3A-C_5A_3. Hence though the original mix composition is such that it can be made up of the three solids C_3S, C_3A, and C_2S, the separation which occurs on clinkering produces a liquid which contains too little lime to give these three solids ; this liquid if allowed to crystallise alone would, as can be shown from a consideration of the crystallisation path, produce the three solids C_2S, C_3A, and C_5A_3 into whose composition triangle it falls. The action of clinkering has thus divided the original mix into a solid containing a higher proportion of lime than the original mix and a liquid containing a lower proportion. It can be shown from a consideration of the crystallisation paths that any original mix around K will at complete equilibrium give the solids C_3S, C_2S, and C_3A ; it is therefore evident that during cooling, and before complete solidification occurs, the liquid must react with the existing solid to remedy the deficiency in its lime content. Thus if equilibrium is maintained the cooling process is not a simple crystallisation of the liquid, but includes a complex process in which solid C_3S dissolves in the liquid and C_2S is deposited out. The extra lime made available in this way enables the liquid to crystallise to yield C_2S and C_3A instead of C_2S, C_3A, and C_5A_3. This complex change on cooling must occur at the invariant point E. That such a change could occur during the short time available while the clinker cools under the conditions of Portland cement manufacture is improbable. In consequence the liquid must crystallise as a separate liquid to yield the compounds mentioned (i.e., C_2S, C_3A and C_5A_3) or, if cooling is too rapid, it may form a glass.

These considerations have led a number of investigators[10] to the conception that Portland cement is a material in frozen, or quenched, equilibrium—that is,

equilibrium is established (or nearly established) at the clinkering temperature, but is fixed on cooling from this point. The compound content of the cooled clinker is then made up of the amounts of the solid compound present at the clinkering temperature together with the products yielded by the liquid as it cools without reacting appreciably with the pre-existing solid. The amounts

TABLE I.

COMPARISON OF COMPOUND CONTENTS IN THE SYSTEM $CaO-C_2S-C_5A_3$.

	Crystallisation to complete equilibrium (Bogue calculation).	Equilibrium frozen from clinkering temperature.	
		Liquid crystallises independently.	Liquid forms glass.
$3CaO.SiO_2$	52	66	66
$2CaO.SiO_2$	22	11	3
Glass	0	0	31
$3CaO.Al_2O_3$	26	15	0
$5CaO.3Al_2O_3$	0	8	0

of the compounds thus present can only be obtained by use of the data afforded by phase equilibrium diagrams, and in general differ from that given by the simple Bogue formula which assumes complete equilibrium during cooling. As an illustration we may consider (Fig. 2) a mix of composition (v), CaO 68.9, SiO_2 21.3, Al_2O_3 9.8, which at a clinkering temperature of 1500 deg. will be made up* of solid C_3S and C_2S and the liquid (ii). The variation of compound content in the cooled clinker according as equilibrium is completely maintained, or is frozen from the clinkering temperature, is illustrated by Table I. The two cases that the liquid crystallises separately and independently of the pre-existing solid, and that it fails to crystallise and forms a glass, are considered for the frozen equilibrium. It is seen for this case, which is fairly typical, that the tricalcium silicate content calculated by the Bogue formula is 14 per cent. lower than the value obtained when the clinker equilibrium is frozen.

There is still another point which emerges if we consider further the conception of the frozen equilibrium. The mix represented by the point (vi), Fig. 2, at 1500 deg. will be made up of a liquid of composition given by point (i) lying on the $CaO-C_3S$ boundary and solid CaO and C_3S†. Some free lime thus exists at the

* The original mix composition, the composition of the liquid, and the mean composition of the solids formed must lie on a straight line. For any liquid composition on the 1500 deg. C. contour over the C_3S primary phase field (i.e., over the line i-ii) a line drawn from the liquid composition through the original mix composition (v) intersects the side of the triangle between the C_3S and C_2S composition points. These two compounds must therefore both be present in the solid ; the liquid composition must then lie on the C_3S-C_2S boundary line where it is intersected by the 1500 deg. contour, i.e., at point (ii).

† A line drawn from any point on the 1500 deg. contour in the C_3S primary phase field (i.e., on the line i-ii) through the original mix composition (vi) intersects the side of the triangle between the CaO and C_3S composition points. These two compounds must therefore be present in the solid and the liquid composition must lie on the $CaO-C_3S$ boundary line at 1,500 deg., i.e., at point (i).

clinkering temperature as a solid in equilibrium with the liquid, and no extension of the time of heating at 1500 deg. would make it disappear. A consideration of the crystallisation path shows that if equilibrium is maintained during cooling this solid CaO will disappear by redissolving in the liquid as the temperature falls, and finally the solids C_3S, C_2S and C_3A, into whose composition triangle point (vi) falls, would result. Since, however, such a reaction will not occur if

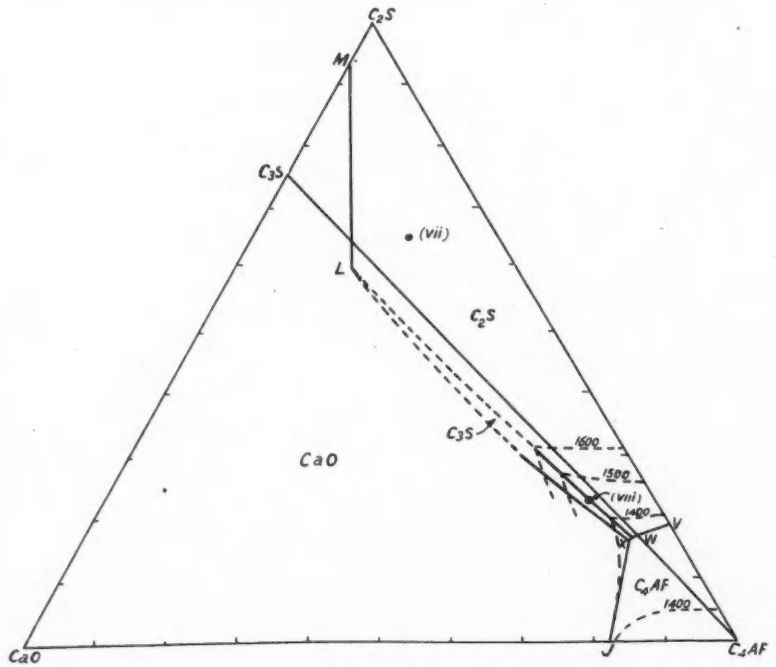

Fig. 3.—System CaO–2CaO.SiO_2–4CaO.Al_2O_3.Fe_2O_3.

the equilibrium existing at the clinkering temperature is frozen, some free lime will appear in the product even though the original mix contains less lime than is required to form C_3S and C_3A. It is therefore generally considered that in any mix which at the clinkering temperature gives a liquid falling on the CaO-C_3S boundary, and a solid containing free CaO in equilibrium with it, the free CaO will remain in the cooled clinker. The maximum amount of lime which can be combined in a lime-alumina-silica mix under Portland cement clinkering conditions is thus not that required to form $C_3S + C_3A$, but a lesser amount corresponding to the condition that no liquid falling on the CaO-C_3S boundary shall be formed. In the CaO-Al_2O_3-SiO_2 system this limit is given by a line from the

C_3S composition point to D. Any mix falling on the high-lime side of this line contains more lime than can be combined under normal clinkering conditions.

In the foregoing discussion we have considered the system $CaO\text{-}Al_2O_3\text{-}SiO_2$, and we have now to consider the effect of the introduction of ferric oxide into the mix. Before passing on to the quaternary system it is convenient first to discuss another ternary system $CaO\text{-}2CaO.SiO_2\text{-}4CaO.Al_2O_3.Fe_2O_3$ made up by substituting C_4AF for C_5A_3 as one of the components. This system has been found to be a true ternary system ; that is, any mix made up from these three compounds yields on melting only liquids and solids whose compositions can be represented in terms of the three component compounds. The compound C_4AF has a ratio of Al_2O_3/Fe_2O_3 of 0.64, and all mixes in this ternary system will have this alumina-ferric oxide ratio. The system $CaO\text{-}C_2S\text{-}C_5A_3$ containing no ferric oxide has an alumina-ferric oxide ratio of infinity. All commercial Portland cements have Al_2O_3/Fe_2O_3 ratios falling between these values of infinity and 0.64, so that the two ternary systems in effect bracket the Portland cement composition zone.

The phase equilibrium diagram for the system[1] $CaO\text{-}C_2S\text{-}C_4AF$ is shown in Fig. 3. The diagram bears many resemblances to that of the system $CaO\text{-}C_2S\text{-}C_5A_3$, and the C_3S field in both takes the form of a long thin area. There is, however, one very important difference. In the system $CaO\text{-}C_2S\text{-}C_5A_3$ the C_3S field lies on the low-lime side of the $C_3S\text{-}C_3A$ composition line, and the lower portion of it, with which we are concerned in Portland cement equilibria, lies on the low-lime side of the $C_2S\text{-}C_3A$ composition line. The effect of this, as has been seen, is to cause a splitting at the clinkering temperature of a lime-alumina-silica mix of Portland cement composition into a more highly basic solid and a liquid of much reduced lime content. In the system $CaO\text{-}C_2S\text{-}C_4AF$, however, the C_3S field lies entirely on the high-lime side of the $C_3S\text{-}C_4AF$ composition line. Mixes in this system corresponding to Portland cement compositions fall in the $C_3S\text{-}C_4AF\text{-}C_2S$ triangle in a region around the point (vii), Fig. 3. On heating to a clinkering temperature they will form, when equilibrium is attained, liquids falling along the $C_3S\text{-}C_2S$ boundary WL and solid C_3S and C_2S. Thus at a clinkering temperature of 1450 deg. a mix of composition (vii) forms solid C_3S and C_2S and a liquid (viii)†. This liquid falls into the triangle $CaO\text{-}C_3S\text{-}C_4AF$ and, if it crystallises alone without reaction with any pre-existing solid, it will yield these three compounds. It is therefore evident that the effect of clinkering on mixes in this system is to split the original mix into a liquid containing an increased proportion of lime and a solid containing a decreased proportion ; this is the reverse of what happened in the $CaO\text{-}C_2S\text{-}C_5A_3$ system. Applying as before the conception of an equilibrium frozen from the clinkering temperature we at once obtain two very interesting results. In the first place, a mix of any lime content falling in the triangle $C_3S\text{-}C_2S\text{-}C_4AF$ will form a liquid which contains an excess of lime, and which on crystallisation without any reaction with the pre-existing solid phase must produce some free lime. It is therefore evident

† This can be shown by similar considerations to those given in the footnote to page 35.

that under clinkering conditions all mixes in this system must produce products containing free lime. The amount of this free lime, however, does not exceed about 0.6 per cent. for any Portland cement composition falling in the C_3S-C_2S-C_4AF triangle. If we disregard this small amount of free lime we can in this system then take the C_3S-C_4AF lime as defining the maximum lime content which can be combined in a cement clinker.

TABLE II.

COMPARISON OF COMPOUND CONTENTS IN SYSTEM CaO-C_2S-C_4AF.

	Crystallisation to complete equilibrium.	Equilibrium frozen from clinkering temperature.	
		Liquid crystallises independently.	Liquid forms glass.
$3CaO.SiO_2$	53	50.4	41
$2CaO.SiO_2$	25	27	27
Glass	0	0	32
$4CaO.Al_2O_3.Fe_2O_3$ ..	22	22	0
Free CaO	0	0.6	0

It follows in the second place that the solid existing at the clinkering temperature must be deficient in C_3S, since the liquid is high in lime. If equilibrium were maintained during cooling some solid C_2S would dissolve in the liquid, combine with the excess lime, and separate out again as C_3S, so causing the whole mix to crystallise to the complete equilibrium compound content. In the frozen equilibrium this does not occur. A comparison of the compound contents of the mix (vii) (Fig. 3), ($CaO = 65.4$, $SiO_2 = 22.7$, $Al_2O_3 = 4.6$, $Fe_2O_3 = 7.3$), when crystallised to yield its complete equilibrium products and when the equilibrium is frozen and the liquid crystallises without reaction with any pre-existing solid, or fails to crystallise and forms a glass, is shown in Table II.

It is seen in this case that the C_3S content calculated for complete equilibrium is 3 per cent. higher than that obtained in the frozen equilibrium with liquid crystallising, and 12 per cent. higher than that obtained if a glass is formed. A comparison of Tables I and II shows that the two cements which give almost identical C_3S contents by the Bogue calculation* may differ in their actual contents by up to 25 per cent.

The two ternary systems we have considered with Al_2O_3/Fe_2O_3 ratios of infinity and 0.64 lie on either side of the range of Portland cement compositions; for these the Al_2O_3/Fe_2O_3 ratio varies between extreme limits of about 12 for white cements to about 0.8 for some recent low-heat Portland cements†. The alumina-ferric oxide ratio is clearly a factor of much importance in determining the devia-

* The Bogue calculation applied to the mix of Table II would yield the values given under "Liquid crystallises independently" if the free lime was estimated and allowance made for it.

† The German Erz cement has still higher iron content and falls outside the composition regions considered in this paper.

tion of the actual compound content of Portland cements from the values given by the Bogue formula. Neither of the two ternary systems we have considered is adequate to define the condition of Portland cement, and a knowledge of the quaternary system CaO-Al_2O_3-SiO_2-Fe_2O_3 is required. The results derived even from this system do not completely represent Portland cement since the remaining minor components are omitted, but they permit of a much closer approximation to the truth than do the ternary systems.

The Quaternary System—CaO-C_2S-C_5A_3-C_4AF.

The quaternary system CaO-Al_2O_3-SiO_2-Fe_2O_3 covers a range of compositions far wider than those which are of interest in the study of Portland cement, and we need only to consider a small portion of the whole system. The quaternary

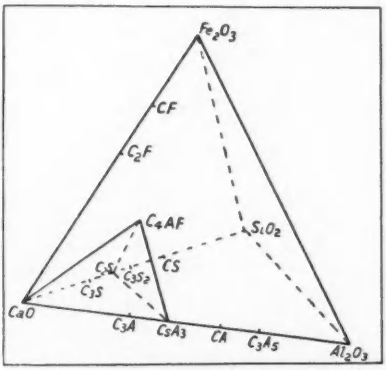

Fig. 4.—Relationship of the System CaO–$2CaOSiO_2$–$5CaO.3Al_2O_3$–$4CaO.Al_2O_3.Fe_2O_3$ to the Larger System CaO–Al_2O_3–SiO_2–Fe_2O_3.

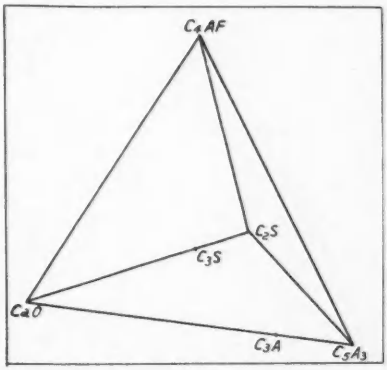

Fig. 5.—Outline of System CaO–C_2S–C_5A_3–C_4AF.

system CaO-C_2S-C_5A_3-C_4AF which covers the compositions of all solids and liquids formed in the clinkering of Portland cement (so far as the four oxides CaO, Al_2O_3, SiO_2, Fe_2O_3 are concerned) is a complete quaternary system within the larger system and is sufficient for our purpose. The relation of this smaller system to the larger one is shown in Fig. 4, while Fig. 5 shows the outline framework of the smaller system treated as an independent quaternary system.

In a ternary system the composition of any mixture of the three components is represented by a point in an equilateral triangle, the apices of which each represents one of the three pure components. The composition of any mixture in a quaternary system can similarly be represented by a point in a regular tetrahedron, the four apices of which each represents one of the four pure components. The side faces of the regular tetrahedron each consists of one of the four bounding ternary systems. Thus in Fig. 5 the quaternary system CaO-C_2S-C_5A_3-C_4AF has as its four bounding faces the ternary systems CaO-C_2S-C_5A_3,

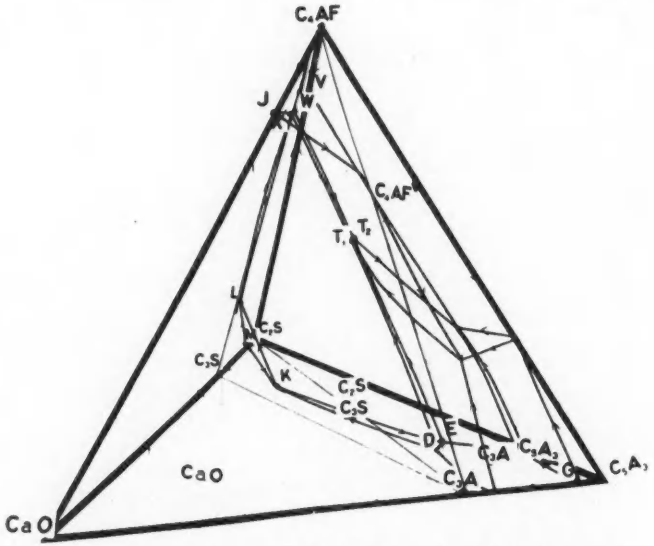

Fig. 6.—System CaO–2CaO.SiO_2–5CaO.3Al_2O_3–4CaO.Al_2O_3.Fe_2O_3.

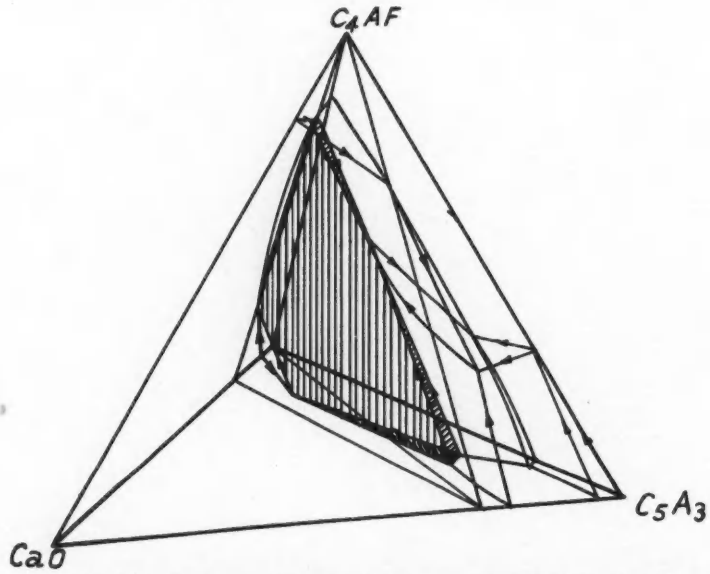

Fig. 7.—The Quaternary System CaO–C_2S–C_5A_3–C_4AF Showing the C_3S Primary Phase Volume Shaded.

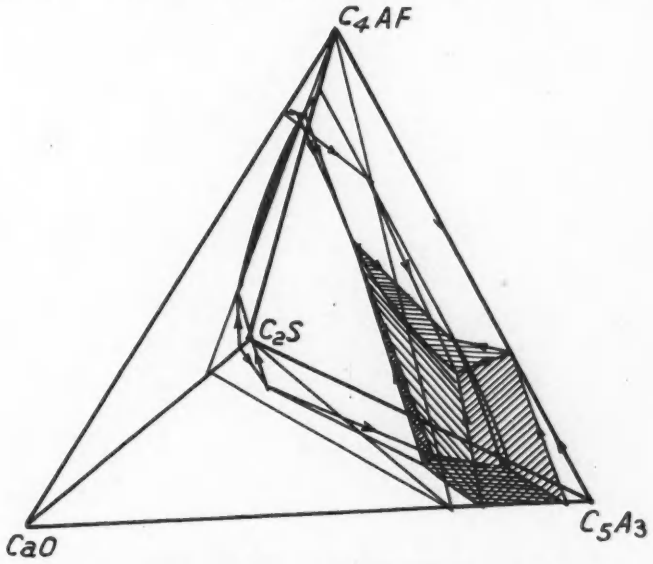

Fig. 8.—The Quaternary System CaO–C_2S–C_5A_3–C_4AF Showing the C_3A Primary Phase Volume Shaded.

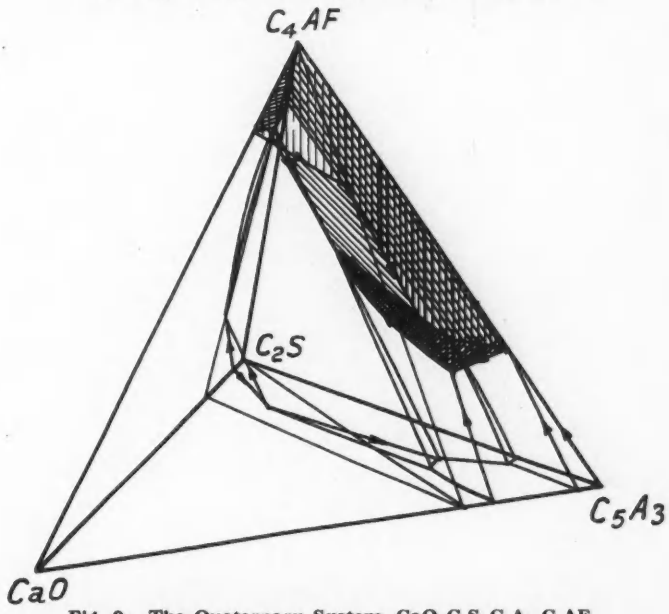

Fig. 9.—The Quaternary System CaO–C_2S–C_5A_3–C_4AF Showing the C_4AF Primary Phase Volume Shaded.

CaO-C_2S-C_4AF, CaO-C_5A_3-C_4AF[5] and C_2S-C_5A_3-C_4AF[1]. The first two of these ternary systems have already been discussed as limiting cases for Portland cement compositions. The equilibrium diagrams for the remaining two ternary systems are also known. The complete equilibrium diagram[1] for the quaternary system is given in Fig. 6, which is a photograph of a model, and also in Figs. 7, 8, and 9, in which the primary phase volumes of C_3S, C_3A and C_4AF respectively are shown shaded. The significance of the various lines is most easily appreciated by considering the development of a ternary into a quaternary system. The base plane of Fig. 6 is the ternary system CaO-C_2S-C_5A_3 which has previously been seen in Fig. 2. The primary phase field of C_3S is represented by the plane area KDE in this ternary system, but in the quaternary system it becomes a primary phase volume stretching upwards from the base (*see* Fig. 7). This volume now represents for the quaternary system the range of liquid compositions from which C_3S is the first solid to separate on cooling. The boundary curve KD becomes a bounding surface of this C_3S primary phase volume, and the other boundary curves similarly form other surfaces. The invariant points, such as D and E, become lines marking edges of the C_3S primary phase volume. There also appear new invariant points as T_1 and T_2; these are points at which four solids and a liquid can exist together in equilibrium at a single temperature and liquid composition. The C_3S primary phase volume is a volume bounded on the high-lime side by the surface KDT_1XLK; at any liquid composition represented by a point on this surface, and at the corresponding temperature, the two solids CaO and C_3S can co-exist in equilibrium with the liquid, just as they do on the boundary curve KD in the base ternary system of Fig. 2. On the low-lime side the volume is bounded by the surface KET_2WLK which represents liquid compositions over which C_3S and C_2S can exist together. The surface DET_2T_1 similarly represents the liquid compositions over which C_3S and C_3A can exist together in equilibrium with liquid, and the surface XWT_2T_1, that for C_3S and C_4AF. The lines DT_1 and ET_2 are lines of liquid compositions with which the three solids CaO, C_3S, C_3A and C_2S, C_3S, C_3A can exist in equilibrium; the lines XT_1 and WT_2 have a similar significance for CaO, C_3S, C_4AF and C_2S, C_3S, C_4AF. The point T_1 is the invariant point at which liquid of the composition represented by T_1 and the four solids CaO, C_3S, C_3A, C_4AF can exist together at a definite temperature; T_2 is the corresponding point for the four solids C_2S, C_3S, C_3A, C_4AF. The points T_1 and T_2 have the temperatures 1341 deg. and 1338 deg. C. The temperatures vary along all the lines and boundary surfaces, and could if desired be represented in the model by a system of contouring. For simplicity it suffices to indicate by arrows the direction of fall in temperature along the lines. There are numerous other considerations arising from the quaternary model which might be discussed, but the points mentioned will be adequate for the present treatment.

The compounds appearing in the quaternary system are the same as those on the bounding ternary planes, and no new compounds are formed. The conclusions which had previously been drawn from ternary systems as to the compounds present in Portland cement are thus confirmed.

The region of Portland cement compositions in this model is a volume centred roughly around the line KL. On clinkering any such mix it forms, when equilibrium is reached, a solid composed of C_3S alone, C_2S and C_3S, or CaO and C_3S, and a liquid which falls within the C_3S primary phase volume or on its boundary surface with C_2S or CaO. Normally all the alumina and ferric oxide in the mix will have passed into the liquid, and the ratio Al_2O_3/Fe_2O_3 in this liquid must

TABLE III.

COMPARISON OF COMPOUND CONTENTS IN SYSTEM $CaO-C_2S-C_5A_3-C_4AF$.

	Crystallisation to complete equilibrium (Bogue calculation).	Equilibrium frozen from clinkering temperature.	
		Liquid crystallises independently.	Liquid forms glass.
1.—CaO = 68 per cent. : SiO_2 = 23 per cent. : Al_2O_3 = 7 per cent. : Fe_2O_3 = 2 per cent.			
$3CaO.SiO_2$	52	60	60
$2CaO.SiO_2$	27	21	15
Glass	0	0	25
$3CaO.Al_2O_3$	15	9	0
$4CaO.Al_2O_3.Fe_2O_3$ ..	6	6	0
$5CaO.3Al_2O_3$	0	4	0
2.—CaO = 68 per cent. : SiO_2 = 23 per cent. : Al_2O_3 = 6 per cent. : Fe_2O_3 = 3 per cent.			
$3CaO.SiO_2$	57	60	60
$2CaO.SiO_2$	23	21	16
Glass	0	0	24
$3CaO.Al_2O_3$	11	9	0
$4CaO.Al_2O_3.Fe_2O_3$ ..	9	9	0
$5CaO.3Al_2O_3$	0	1	0
3.—CaO = 67 per cent. : SiO_2 = 23 per cent. : Al_2O_3 = 4 per cent. : Fe_2O_3 = 6 per cent.			
$3CaO.SiO_2$	63	60.7	55
$2CaO.SiO_2$	18	20	20
Glass	0	0	25
$3CaO.Al_2O_3$	1	1	0
$4CaO.Al_2O_3.Fe_2O_3$ ..	18	18	0
Free CaO	0	0.3	0

therefore be the same as in the original mix. It is possible with the aid of this ratio for any clinkering temperature to fix the composition of the liquid. There are some white Portland cements of very high alumina-ferric oxide ratio for which the clinkering temperature may occasionally not be high enough to cause all the alumina to pass into the liquid. The liquid composition in such cases would fall on the boundary surface of C_3S and C_3A (DET_2T_1).

We have seen in the case of the ternary systems $CaO-C_2S-C_5A_3$ and $CaO-C_2S-C_4AF$ that, if equilibrium is to be maintained between liquid and solid

during cooling from the clinkering temperature, it is necessary for a reaction to occur between them. It has been shown that if this reaction fails to occur and the equilibrium is frozen from the clinkering temperature, as is to be expected in practice, the compound content of the cooled clinker may differ considerably from that calculated on the assumption of complete equilibrium during cooling. The same considerations apply to the quaternary system, and we are now in a position to calculate from the data relating to it the clinker composition corresponding to the frozen equilibrium for cements of any alumina-ferric oxide ratio.

It will be necessary in order to do this to fix a clinkering temperature, and the value of 1400 deg. C. will be adopted. It should be noted, however, that as the amount and composition of the clinker liquid changes only very slowly with temperature above 1400 deg. C. the results would not be much affected if a temperature 50 to 100 deg. higher had been selected. In Table III are shown the compound contents of some typical Portland cement clinkers of various alumina-ferric oxide ratios, (1) when calculated for complete equilibrium on cooling (Bogue calculation) and (2) for the frozen equilibrium for the two conditions that the liquid does and does not crystallise.

It will be observed that the differences between the values for the frozen equilibria and the Bogue calculation values are not so serious as was found for the ternary systems in Tables I and II, but that the differences may still be considerable. In general the C_3S content calculated from the Bogue formula is lower than the value corresponding to the conditions of frozen equilibrium when the Al_2O_3/Fe_2O_3 ratio is high, and the reverse when the ratio is low. At some intermediate ratios they will closely agree. Methods and data by which the deviations from the Bogue values may be calculated for any composition are given in the complete report on this work appearing as a Building Research Technical Paper (No. 16).

The difficulty still remains that the relative extent to which the liquid in a clinker has crystallised cannot usually be determined, and it is not possible therefore to differentiate between the two alternate cases that the liquid crystallises or forms a glass. This would not be important if the properties of glass and crystal phases of the same gross composition were closely similar, but it seems very doubtful whether such will be the case. No information is at present available on this problem of the relative properties of glass and crystal phases.

Maximum Lime Content of Portland Cements.

It was seen in the earlier part of this paper that the maximum amount of lime which could be combined under clinkering conditions was determined by the condition that uncombined lime should not appear at the clinkering temperature as a solid in equilibrium with the liquid. An analysis of the model for the quaternary system shows that this condition holds for all mix compositions lying on the low-lime side of the plane determined by the two composition points C_3S and C_4AF and by the point D in the base plane of Fig. 6. This is not an exact description of the limiting surface, but it is sufficient for practical purposes.

It can be calculated from the position of this plane that the maximum lime content is given by the equation

$$CaO = 2.8SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3.$$

This formula, which has a definite theoretical basis, is very similar to empirical formulæ proposed by Kühl[11] and Spohn.[12] It is applicable to all Portland cements with an alumina-ferric oxide ratio not less than 0.64. Its application in practice can most easily be tested by examining the amount of combined lime present in commercial Portland cements. This has been done for some 150 cements, and the results obtained with those containing the highest combined lime contents are shown in Table IV. The total lime content of the cement as

TABLE IV.

COMBINED LIME CONTENTS OF SOME HIGH LIME CEMENTS.

1 Cement No.	2 Lime—Lime in $CaSO_4$.	3 Free lime.	4 Actual combined lime.	5 Theoretical maximum lime.	6 Actual combined lime / Theoretical maximum lime.	7 British hydraulic modulus.
1	63.9	3.7	60.2	62.5	0.965	3.01
2	62.4	4.2	58.2	60.9	0.97	3.03
3	64.0	2.8	61.2	62.2	0.985	3.12
4	63.2	1.9	61.3	62.4	0.985	3.02
5	65.6	2.9	62.7	63.2	0.99	3.04
6	59.9	0.5	59.4	59.6	0.995	2.96
7	61.2	2.0	59.2	59.2	1.00	3.05

determined by analysis has been corrected for the lime combined with sulphur tri-oxide as gypsum and the resultant value is shown in column 2. The free lime content determined by the glycerol method [13] is shown in column 3, and the content of lime actually combined in the cement, obtained by the difference of columns 2 and 3, is shown in column 4. The theoretical maximum lime content calculated from this equation using the contents of SiO_2, Al_2O_3 and Fe_2O_3 determined from the analysis of the cements is shown in column 5. The British hydraulic modulus calculated as laid down in the British Standard Specification for Portland Cement[14] is tabulated in column 7 and shows that the lime content in all but one case exceeds the British Standard Specification limit. It will be observed that, though the available lime content given in column 2 exceeds the theoretical maximum lime content by up to 2½ per cent., the actual combined lime content never exceeds the theoretical value but in one case actually equals it. Since no account of the minor components such as MgO*, alkalis and titania is taken the formula cannot hold rigidly, but as a practical working limit it seems satisfactory.

* There is evidence, as mentioned earlier, that most of the MgO in Portland cement is uncombined.

Liquid Contents of Clinkers

It is possible with the aid of the data available from the quaternary system CaO-C_2S-C_5A_3-C_4AF to calculate the amount of liquid formed on clinkering any mix of Portland cement compositions of the oxides CaO, Al_2O_3, SiO_2, Fe_2O_3 with Al_2O_3/Fe_2O_3 ratio not less than 0.64. The liquid which is formed on clinkering must fill the interstices between the solid grains which exist at the clinkering temperature, binding them together in the typical clinker pellet. An examination of thin sections of cement clinkers shows that this liquid, whether it crystallises or not on cooling, remains as interstitial matter surrounding the primary grains of C_3S and C_2S (see Fig. 10). It should therefore be possible by microscopic

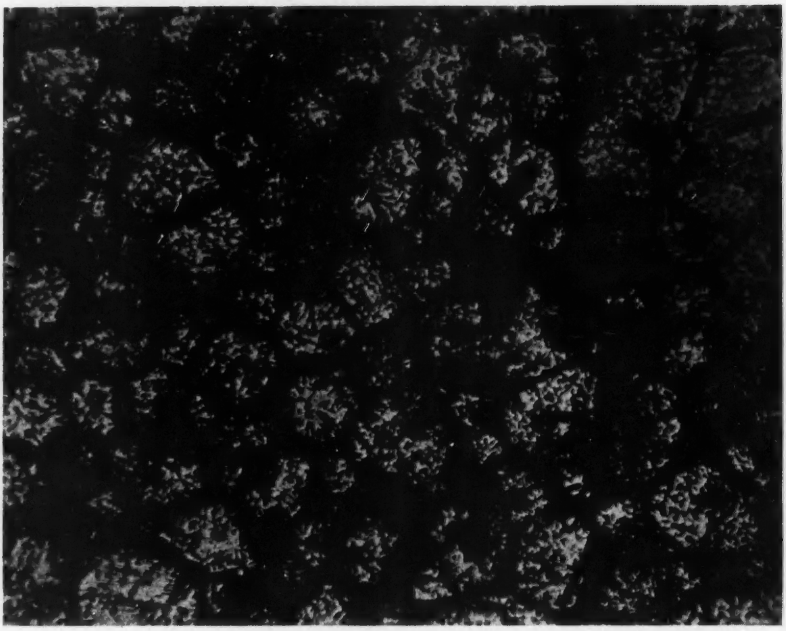

Fig. 10.—Thin Section of Portland Cement Clinker showing dark Interstitial Materials surrounding Primary Crystals (×350).

measurements on thin sections of clinkers to estimate the amount of liquid formed on clinkering. A check on this method has been made using CaO-Al_2O_3-SiO_2-Fe_2O_3 mixes, and it has been found that the content of liquid so determined agrees well with the value calculated from the data on the quaternary system. The method can only be applied satisfactorily on the better burnt clinkers with the higher liquid contents, as on clinkers of low liquid content the size of the primary crystal grains becomes very small and measurement with reasonable

accuracy of the interstitial matter becomes very difficult. An application of this method has made it possible to study the influence of the minor components, magnesia and the alkalis, on the amount of liquid formed in mixes of the four main oxide components CaO, Al_2O_3, SiO_2, Fe_2O_3. It has been found that the increase in liquid formation at normal clinkering temperatures is only of the order of the amount of alkalis and magnesia present. The amount of liquid formed in any commercial cement mix on clinkering at a defined temperature can then be calculated from the CaO, Al_2O_3, SiO_2, Fe_2O_3 contents with the aid of the quaternary system data, and a rough correction for other minor components made by adding their total content to the amount of liquid calculated. Whilst this correction is only a rough approximation which may be replaced later by more accurate formulæ, the error introduced in the liquid content will not be very large since the amount of the minor component is usually small, 2 to 5 per cent. in all, compared with total liquid contents which vary from 15 to 30 per cent.

Calculations from the analyses of some 150 Portland cements for an arbitrary clinkering temperature of 1400 deg. show contents of liquid formed on clinkering varying from 15 to 22 per cent. for white Portland cements and from 17 to 35 per cent. for grey Portland cements. As the rate of increase of liquid content above 1400 deg. C. is small the data will not be appreciably affected by the assumption of higher clinkering temperatures. At lower clinkering temperatures, however, the liquid contents fall away at rates which depend, as shown later, on the composition of the mix. Microscopic measurements on thin sections of well burnt commercial clinkers show that liquid contents from 25 to 30 per cent. have been formed on clinkering. The value for the less well burnt clinkers cannot easily be measured for the reason already stated, but they must be lower.

It is of interest to examine how the amount of liquid formed on clinkering varies with the composition of the mix and the temperature. The initial temperature at which liquid formation commences is about 1280 deg. C. for any Portland cement[15]; the amount of liquid formed at this and successively higher temperatures varies much with the mix composition. In Table V are given data for mixes of various alumina and ferric oxide contents and ratio. A constant content of 3 per cent. magnesia and alkalis is taken in all the mixes. The ratio of lime to silica has no appreciable effect on the amount of liquid formed, and it is only the sum of the two which is of importance in this connection. This does not imply that an increase in the CaO : SiO_2 ratio will not tend to render the attainment of complete combination more difficult, for more lime has to be combined in the solid formed at the clinkering temperature.

Table V shows that the amount of liquid formed at 1338 deg. C. (the temperature of the invariant point C_3S-C_2S-C_3A-C_4AF in the quaternary system CaO-Al_2O_3-SiO_2-Fe_2O_3) increases as the sum of alumina and ferric oxide contents is increased, and also as the Al_2O_3/Fe_2O_3 ratio is decreased, at constant sum, down to a ratio of 1.38. At 1400 deg. C. and above it increases as the sum of the alumina and ferric oxide increases, but decreases slightly as the Al_2O_3/Fe_2O_3 ratio decreases.

The full value of these data can only be worked out in combination with the results of practice, but there are certain points to which attention may at this stage be drawn. The range of temperatures available for clinkering any cement mix must, it seems, be bounded on one side by a minimum liquid content necessary for adequate combination to occur, and a coherent clinker to be formed, and on the other side by the maximum content which can be tolerated without serious ringing or balling occurring. It is probable that the viscosity and surface tension of the liquid, as well as the amount, must be important factors, but no information is available regarding them.

TABLE V.

VARIATION OF LIQUID CONTENTS OF CLINKERS WITH TEMPERATURE.

$CaO+SiO_2$	$\frac{Al_2O_3}{Fe_2O_3}$	Al_2O_3	Fe_2O_3	MgO and alkalis.	Per cent. liquid.			
					1280 deg. C.	1338 deg. C.	1400 deg. C.	1450 deg. C.
92	9.0	4.5	0.5	3	Point of initial melting.	6.1	17.4	17.6
91	11.0	5.5	0.5	3		6.1	20.0	20.6
	3.0	4.5	1.5	3		12.2	19.6	19.9
	2.0	4.0	2.0	3		15.2	19.2	19.5
	1.38	3.5	2.5	3		18.2	18.8	19.1
	0.8	2.65	3.35	3		6.7	18.2	18.5
89	3.0	6.0	2.0	3		15.2	25.1	25.5
	2.0	5.33	2.66	3		19.2	24.6	25.0
	1.38	4.65	3.35	3		23.4	24.1	24.5
	0.8	3.55	4.45	3		8.9	23.3	23.6
87	3.0	7.5	2.5	3		18.2	30.8	31.1
	2.0	6.66	3.33	3		23.3	30.0	30.5
	1.38	5.80	4.20	3		28.6	29.5	29.9
	0.8	4.45	5.55	3		10.5	28.3	28.9
85	3.0	9.0	3.0	3		21.3	36.2	36.8
	2.0	8.0	4.0	3		27.4	35.4	36.0
	1.38	6.95	5.05	3		33.8	34.6	35.2
	0.8	5.3	6.7	3		11.4	33.3	34.0

A clinker in which the liquid content mounts rapidly to a high value will have a shorter clinkering range than one in which the increase is more gradual. It seems, therefore, that in mixes such as those of 10 to 12 per cent. Al_2O_3 and Fe_2O_3 in which the liquid content at 1338 deg. C. is high, the progressive substitution of ferric oxide for alumina will shorten the clinkering range. If this substitution is carried past the ratio $Al_2O_3/Fe_2O_3 = 1.38$ the amount of liquid formed at 1338 deg. C. is much decreased, but for such mixes there is a very rapid increase in liquid content just above 1338 deg. C. and little or no real increase in the clinkering range is to be anticipated. In mixes containing less alumina and ferric oxide no such effect might be noticeable because of the much lower liquid content formed at 1338 deg. and its subsequent slow increase. It will also be evident that in mixes in which the total amount of the sesquioxides

is low, as in many white Portland cements, only a low liquid content is obtainable at any temperature that can be reached under commercial conditions in the rotary kiln. This is probably the reason why many white Portland cements show high free lime contents even though the lime-silica ratio is not high.

Summary.

The application to cement technology of constitutional work on Portland cement is discussed with reference first to the ternary systems $CaO\text{-}2CaO.SiO_2\text{-}5CaO.3Al_2O_3$ and $CaO\text{-}2CaO.SiO_2\text{-}4CaO.Al_2O_3.Fe_2O_3$ and then to the quaternary system $CaO\text{-}2CaO.SiO_2\text{-}5CaO.3Al_2O_3\text{-}4CaO.Al_2O_3.Fe_2O_3$. The phase equilibrium diagrams are considered, and it is shown that the results on the quaternary system confirm the conclusions that have been drawn from the ternary systems regarding the compounds which are present in Portland cement. The conception of Portland cement as a material whose equilibrium is frozen from the clinkering temperature is discussed, and the effect of this on the contents of the various compounds present in Portland cement described. It is shown that the calculation of the compound content on the assumption that the cooled clinker is in complete equilibrium is subject to an error which varies with the alumina-ferric oxide ratio of the mix.

The maximum amount of lime which can be combined in Portland cement is derived and found to be in good agreement with results in practice.

The effect of clinkering temperature and cement composition on the amount of molten liquid formed during clinkering is illustrated by calculations, and its bearing on cement production under rotary kiln conditions considered.

The author wishes to express his thanks to Mr. B. H. Wilsdon for very helpful discussion and criticism of the methods of presentation adopted in this paper.

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The Setting Time of Portland Cement.

By W. WATSON, B.Sc., and Q. L. CRADDOCK, M.Sc.

STRICTLY speaking, Portland cement cannot be said to possess a definite setting time as the process is a continuous one and in all probability continues well into the hardening period. In practice it is convenient to fix an arbitrary setting time, i.e., the stiffening of the pasty mass, and the time occupied in reaching this point from the moment of mixing the cement with water is the setting time.

Methods of Determining Setting Time.

The following are the usual methods of determining setting time:

(1) Mechanical, by means of Vicat or Gilmore needles.—These methods are explained fully in text-books on cement and it is therefore unnecessary to describe them here. Automatic machines have also been devised on the principle of these instruments.

(2) Thermal.—This method consists in gauging the cement with water and recording the change in temperature with time. At the point of initial set the temperature curve shows a sharp rise and when the final set is reached the temperature gradually falls. This method is not particularly accurate as the points at which the slope of the curve changes are dependent as much upon chemical composition and fineness as upon the setting properties of the cement.

(3) Electrical.—If the conductivity of a cement paste is measured during the setting and hardening period, the specimen being maintained at constant temperature, the resistance suddenly changes at the moment corresponding to the final set as defined by the maximum temperature change. The cement paste is contained in a small tube placed in a thermostat. Two platinum electrodes are immersed in the paste and connected to an alternating-current bridge and the changes in resistance are measured in the usual way. The rate of setting and hardening is influenced by changes in temperature but the method is considered better adapted and more accurate than the mechanical and thermal methods.

The time of set is affected by (*a*) The chemical composition of the cement. (*b*) The fineness of the cement and its grain size composition. (*c*) The physical conditions to which it is exposed during (1) clinker formation (e.g., hard or light burning) and rate of clinker cooling; (2) grinding (e.g., quantity of gypsum added), whether the mill is "steamed," and the temperature attained by the cement as it leaves the mill; and (3) storage of cement before testing, e.g., period and condition of storage, extent of aeration, humidity, carbon dioxide content, and temperature of the atmosphere during storage and aeration. (*d*) The temperature of the cement and water used during the gauging of the setting-time pat, the percentage of gauging water used, the humidity, carbon dioxide content, and temperature of the atmosphere surrounding the test-piece. (*e*) The time taken in preparing the setting-time pat.

Influence of Chemical Composition.

When all other factors are considered constant the effect of the chemical composition on the setting-time may be summarised as follows:

(1) Lime ratio or hydraulic modulus. High-limed cements tend to be slow setting. Low-limed cements, especially when the alumina content is high, tend to be quick-setting.

(2) Silica ratio ($\%SiO_2/\%R_2O_3$). When this ratio exceeds 3.0 the cement is usually slow-setting.

(3) Ratio of Al_2O_3 to Fe_2O_3. When the silica ratio does not exceed 2.0, two effects may be observed, (*a*) when Al_2O_3/Fe_2O_3 is high the cement tends to be quick-setting, (*b*) when Al_2O_3/Fe_2O_3 is less than 1.0 the cement tends to be slow-setting.

The effect of all these ratios cannot be considered independently, however, and their united influence must be taken into account.

Substances Lengthening Setting Time.

By passing superheated " dry " steam into a tube mill during grinding Bamber[1] showed that much less than the usual quantity of gypsum was required to produce slow-setting cement. The amount of steam to be used varies with the chemical and physical condition of the clinker and the output required from the mill. Too much steam causes condensation and a coating of partially set cement forms on the sides of the mill. With most cements an absorption of less than 1 per cent. of water by the cement is sufficient. According to Bamber the setting time of a cement retarded by steam is more permanent and less likely to be affected by other factors than cement retarded by an increased quantity of gypsum. Steaming is particularly advantageous where a cement of low SO_3 content is essential. Steam also tends to correct unsoundness, but on the other hand it seems to decrease the strength of the cement and decrease the efficiency of the mill during grinding.

Excess of gauging water will also lengthen the time required for setting. The setting process being one of saturation and formation of either colloids or crystals or both, the time necessary to attain saturation will be lengthened with increased quantities of gauging water.

Gadd[2] has shown that the water of crystallisation of salts mixed with cement can retard setting-time. He pointed out that anhydrous sodium carbonate accelerates the set of cement. Also if the crystalline salt $Na_2CO_3.10H_2O$ is mixed with cement and gauged soon afterwards the set will also be quicker than without additions. As the time between mixing of the crystalline salt with the cement and testing is lengthened, however, the acceleration of the set becomes less marked. After five weeks there is practically no acceleration. Gadd concluded that cement is capable of abstracting water from a dry salt containing water of crystallisation and thereby becoming partially hydrated and slow-setting, but time is required for the process of water extraction to take effect. It is known that in some cases salts containing water of crystallisation lose such water under pressure and reabsorb it when the pressure is removed. Gadd

carried out experiments using quantities of crystalline sodium sulphate and magnesium nitrate such that the water of crystallisation was 2 per cent. of the weight of the cement. The mixtures were then subjected to a pressure of about 4 tons per square inch for six hours. On releasing the pressure and testing the cements the setting time was found to be markedly extended.

Oils retard the set of cement, but are not recommended for use in this connection as they make it very difficult to mix the cement and water and also reduce strength.

Phosphoric acid and phosphates as retarding agents have received considerable attention. Koyanagi[3] stated that monocalcium phosphate if present in large proportions arrests the hydration of the tricalcium aluminate in the cement. It interacts with calcium oxide, originally present in the free state or produced by the hydration of calcium silicate, giving insoluble di- or tri-calcium phosphates. A small proportion of monocalcium phosphate has no injurious effect on setting time. Dahlgreen[4] found that phosphate-bearing gypsum acts more strongly as a retarding agent than ordinary gypsum. Strength at three and seven days is somewhat lowered, but recovery occurs later and the 28-day figure is normal. The use of phosphate-gypsum alone or mixed with ordinary gypsum offers a convenient means of retarding setting time in hot weather. With high-limed cements, however, its use may result in reduced tensile strengths.

Additions of 0.01 per cent. of lead or zinc oxide retard the set, but considerably reduce strength. Cement containing 1 per cent. lead oxide will not harden at all.

It is occasionally noted that cement which has been made slow-setting by the addition of gypsum becomes quick-setting on storage. This can be corrected by the addition of 1 to 2 per cent. of either quick-lime or hydrated lime. CaO or $Ca(OH)_2$ will not, however, retard the set in the absence of gypsum.

Substances Having Little Effect on Setting Time.

Nitrates have little or no effect on setting time. Gadd[2] showed that the only nitrate which has any pronounced effect is crystalline strontium nitrate, which retards the set. The effect of nitrates is much less marked than that of chlorides, sulphates, and carbonates, and in most cases no appreciable alteration of setting time could be observed even with 5 per cent. addition of the salts. He also showed that dry oxygen, dry ozone, and pure dry air have no effect on the setting time of cement exposed to them. Schindler found that dry carbon dioxide had little effect on the time of set. Gadd[2] also showed that cement kept for several months out of contact with the atmosphere (by filling a bottle with cement and sealing), does not materially change in setting time. This constancy is independent of fairly wide fluctuations in temperature and of the action of light during the period of storage. There is, therefore, no apparent spontaneous alteration in chemical composition or physical structure.

Substances Shortening Setting Time.

The finer cement is ground the quicker will be its setting time. Thus a cement ground to about 5 per cent. residue on a 170-mesh sieve and having an

initial set of approximately 3 to 4 hours may quicken up to one hour when ground to less than 1 per cent. residue on the same sieve. The rate of chemical reaction of the cement and water is increased owing to the increased surface exposed.

Mixtures of underburnt and normal or hard-burnt clinkers are apt to be quick setting when ground. No explanation of this appears in the literature, though it is probably to be found in the chemical reaction between the compounds in the two grades of burning. It is evident, however, that uniform burning is essential if the set of the resulting cement is to be regular.

Gadd[2] examined the effect of alkali hydroxides on setting time. He showed that additions of 1.25 per cent. of caustic soda or potash accelerate setting time. Ammonium hydroxide has no effect unless more than 1 per cent. (as NH_3) is present, in which case setting time is also shortened. Calcium hydroxide also accelerates setting time, except in the presence of gypsum as already stated.

Moyer[5] and Cushmann[6] showed that sodium silicate accelerates the set, but this is accompanied by a reduction in strength.

Gadd[2] found that borax, both in the anhydrous and crystalline forms, accelerates setting time, but the latter variety has a much more marked effect than the former. Thus 3 per cent. of $Na_2B_4O_7.10H_2O$ produces a very quick set, while 5 per cent. of the anhydrous salt produces the same effect as 0.5 per cent. of $Na_2B_4O_7.10H_2O$. Carbon dioxide (unless absolutely dry) and the alkali carbonates strongly accelerate the set of cement, 1 per cent. of either Na_2CO_3 or K_2CO_3 being most effective. Acceleration is also produced by the bicarbonates ($KHCO_3$, $NaHCO_3$, $Ca(HCO_3)_2$).

Scottish Dyes, Ltd., Becket, Thomas and White[7] add to the cement or mixing water solid or dissolved ammonium carbonate to quicken the set.

Effect of Aeration of Clinker and Cement.

The setting time can change by exposure to atmospheric air in an erratic manner, being sometimes accelerated and sometimes retarded. Setting time may be differently affected when samples of the same cement are aerated in different localities or for different periods.

Gadd[2, 8] showed that air absolutely free from water and carbon dioxide had no effect upon the setting time of cement exposed to it, but that the absorption of a comparatively small proportion of moist carbon dioxide accelerated the set to a remarkable degree. On the other hand, an absorption of moisture resulted in a retardation of setting time. Further, he found that the set of an originally slow cement could be rendered quick, and again slow, by first exposing the cement to carbon dioxide and then to moist air. The water absorbed by the cement from the atmosphere existed not as free moisture adhering to the grains of cement but as combined water and could not therefore be again expelled by heating at 100 deg. C.

Thus in order to explain the erratic influence of seasoning clinker or cement on setting time we have the following four points to consider: (1) Absorption of water to a marked degree will slow the set. (2) Presence of free lime or the formation of $Ca(OH)_2$ will tend to quicken the set in the absence of gypsum.

(3) Calcium hydroxide in the presence of gypsum will slow the set. (4) Absorption of carbon dioxide will quicken the set. These phenomena seem to account for the varied results which can be obtained when cement is stored ; the humidity and carbon dioxide content of the surrounding atmosphere largely determine the variations in setting time. Some clinkers can be ground alone without gypsum and will produce slow-setting cement. Usually, however, this type of cement becomes quick setting on seasoning. Quick-setting gypsumised cements can often be made slow setting by the addition of hydrated lime as previously stated ; this may be the reason for some quick-setting cements being made slow setting by addition of water to the clinker before grinding.

Influence of Temperature.

Cement sets quicker in hot weather than in cold, the process of hydration being accelerated by rise in temperature. At or about the freezing point of water the setting process is more or less suspended.

Meade[9] stated that if cement is heated for some time at a temperature much above 400 deg. F. it becomes quick setting. This has an important bearing on cement manufacture. When hot clinker is ground (an uneconomic practice), an excessive temperature may be reached in the mill which would tend to make a normal cement quick setting. On the other hand, during the investigation of a consignment of cement which was quick setting even with 2 per cent. SO_3, upon heating it for one hour at 110 deg. C. the cement showed a normal set on cooling. Possibly some water was driven off the gypsum and helped to hydrate the compounds which made the cement quick setting, or else formed calcium hydroxide which in the presence of gypsum had a retarding action.

Influence of Chlorides.

According to Gadd[2] additions of NaCl and KCl up to 2 per cent. appear to have no definite effect on the setting time. On the other hand, Thomas [10] stated that NaCl quickens the set but tends to diminish strength, besides being liable to cause efflorescence ; the plasticity of cement paste is, however, increased by NaCl. Gadd[2] stated that the addition of more than 2 per cent. of NaCl or KCl retards the set, as also does less than 1 per cent. of $CaCl_2.6H_2O$. Acceleration is produced by anhydrous calcium chloride and by more than 1 per cent. of $CaCl_2.6H_2O$. Carpenter[11] found that additions of calcium chloride up to 0.5 per cent. retard the set and larger proportions accelerate it. Uchida[12] found that 3 per cent. calcium chloride accelerates setting time considerably. According to Gadd[2] $MgCl_2$, $BaCl_2$, $BaCl_2.2H_2O$, $SrCl_2$, $AlCl_3.6H_2O$ and $MnCl_2.4H_2O$ accelerate setting time. Crystalline $SrCl_2.6H_2O$ retards setting time. Ferrous and ferric chlorides when present in greater quantities than 2 per cent. accelerate the set ; under 2 per cent. retards the set. Processes have been patented for accelerating the hardening of mortar and cement by the addition of calcium chloride or mixtures containing it. Hinrichsen[13] added HCl, or mixtures of HCl and metallic chlorides, to the mixing water with the object of accelerating the set. Grunau Landshoff and Meyer Co.[14] used a mixture of calcium chloride and aluminium chloride to accelerate the set.

Influence of Sulphates (Other than Calcium Sulphate).

The effect of sulphates is considered on cements ground from pure clinker, i.e., without previous steaming or the addition of gypsum. Gadd[2] found that acceleration of setting time is produced by 5 per cent. or less of K_2SO_4, $MgSO_4$, $FeSO_4$, $FeSO_4.7H_2O$, $Fe_2(SO_4)_3$, $NiSO_4$, $MnSO_4$, $MnSO_4.5H_2O$, $Al_2(SO_4)_3$, $Al_2(SO_4)_3.18H_2O$, $ZnSO_4$, $CoSO_4.7H_2O$, $Cr_2(SO_4)_3.7H_2O$. With ferric sulphate small spots of ferric oxide appeared on the surface of the set cement, indicating chemical action. The process of making a quick-setting composite cement by the addition of a small proportion of ferrous sulphate to Portland cement clinker after burning and before the final stages of grinding has been patented.[15].

Influence of Sodium Sulphide.

Witt[16] found that solutions of sodium sulphide (Na_2S) up to a concentration of 5.9 gr. per litre as a gauging liquid retard the set, maximum retardation being obtained with a solution containing between 0.02 and 0.21 gr. per litre. A solution stronger than 5.9 gr. per litre accelerates the set.

(*To be continued.*)

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Company Registration.

A new company, the Walton and District Sand and Mineral Co., Ltd., was formed on December 6, 1934, to collect " substances of a mineral or other nature used in the formation of cement found lying on the sea-shores of Kirby, Thorpe, and Walton-le-Soken, Essex." The nominal capital of the company is £200, and the only director named is R. W. Chitham, of " Hillcrest," Lower Kirby, Essex.

Resistance of Cements in Corrosive Solutions.

INVESTIGATIONS on the corrosion of cements have usually been carried out on totally immersed specimens, but in a recent number of *Zement* Professor O. Graf states that this method gives misleading results since concretes which are unattacked when tested by total immersion fail in practice when the structure is only partly immersed. Professor Graf describes a series of tests carried out as closely as possible in accordance with practical conditions. Twelve cements were tested, comprising 4 ordinary Portland cements (B, T, L, S), 1 high-strength Portland cement (D), 3 blastfurnace cements (A, V, J), 2 aluminous cements (W, N), and 2 mixed cements (P, Tr), respectively, Portlandjurament and trass cement. The aggregate was Rhine quartz sand of sizes 0.2/1 mm., 1/3 mm., 3/7 mm., 7/15 mm., and 15/30 mm. Two sizes of specimens were used 10 by 10 by 10 cm. and 56 by 10 by 10 cm.

The specimens were placed in the various liquids after 14 days' curing. The prisms were immersed to a depth of 18 cm. and the cubes totally immersed. To observe the effect of agitation of the solution, the solution was stirred by compressed air for one hour morning and evening in some of the tests. Specimens were also cured in solutions in hermetically-sealed containers. The immersion waters used were Stuttgart tap water with 0.9 per cent. Na_2SO_4, 2.1 per cent. Na_2SO_4, 2.4 per cent. $MgSO_4$, and 5 per cent. NaCl ; artificial sea water ; Stuttgart mineral water ; distilled water ; and ordinary Stuttgart tap water. The solutions in the containers for the specimens were renewed after 1, 2, 3, 4, 6, 9, 12, 15, 18, and 21 months. The specimens were tested for appearance of surface, alteration in weight, and bending and compressive strengths. The results obtained are as follow :—

Portland Cement.

SPECIMENS STORED IN 0.9 and 2.1 PER CENT Na_2SO_4.—Corrosion first appeared in the immersed portion as fine cracks at corners and edges, and these grew larger and opened with time. There were also blistering and scaling. Later considerable corrosion occurred at the liquid—air surface, particularly on the tamping face. The corrosion was generally stratified, and was greatest on the outside. Above the surface the salt crystallised out in masses like hoar frost or down.

SPECIMENS STORED IN $MgSO_4$, 2.4 PER CENT. SOLUTION.—The corrosion was largely due to scaling in the portion under the solution. The salt separated out mainly as thick crusts above the liquid level.

SEA WATER.—Fine cracks appeared on the edges, and the separation of salts was less than in the foregoing tests.

5 PER CENT. NaCl.—Only a small amount of salts separated out on the portion in air. No cracks or scaling were observed.

STUTTGART MINERAL WATER.—(CaO, 0.091 per cent. MgO, 0.0071 per cent. SO_3, 0.0927 per cent. Cl, 0.1123 per cent. Na_2O, 0.1048 per cent. CO_2 combined, 0.0454 per cent. ; free, 0.0126 per cent. ; active, 0.0096 per cent.).—No

changes were observed except for a very small separation of salts on the portion in air.

DISTILLED WATER.—No changes.

Blastfurnace Cement.

2.1 PER CENT Na_2SO_4 AND 2.4 PER CENT. $MgSO_4$.—The corrosion was in general the same as for ordinary Portland cement.

SEA WATER.—Cracks formed chiefly at the liquid surface near the edges and only in one of the two cements tested.

5 PER CENT. NaCl.—Only crumbling on the surfaces in air was observed.

STUTTGART MINERAL WATER, DISTILLED WATER, AND STUTTGART TAP WATER. —No changes except for a slight separation of salts were noticed.

Aluminous Cement.

2.1 PER CENT. Na_2SO_4.—At first a considerable separation of salts occurred. Near the liquid—air line small white and yellow grains formed near which the concrete flaked. Later, large cracks appeared chiefly at the liquid—air level and the concrete broke up by scaling. Most of the corrosion occurred in the portion in air.

2.4 PER CENT. $MgSO_4$.—Cracks formed without much weakening of the concrete. If there was corrosion it occurred within a short period of time, hence there is a danger that specimens which show no corrosion at two years may later fail very rapidly.

SEA WATER.—The behaviour was similar to Na_2SO_4.

5 PER CENT. NaCl.—Considerable amounts of white and yellow particles formed on the immersed portions. Apart from a little scaling this portion showed no corrosion. The portion in air, however, fell to pieces.

Mixed Cement.

In Na_2SO_4 and $MgSO_4$ solutions, the corrosion and separation of salts was in general the same as for Portland cement. In mineral water there were no marked changes.

In the case of specimens immersed in Na_2SO_4 solution it was found that by far the greatest concentration of salts occurred at about 1 cm. under the surface of the specimens. Very little salt was found in the centre of the test pieces. For those immersed in $MgSO_4$ solution the largest amount of salt occurred in the immersed portion of the specimen but none was found in the centre portion. In the case of sea water and 5 per cent. NaCl the salt was uniformly distributed through a horizontal section and more salt was found in the portion in air.

Effect of 0.9 and 2.1 Per Cent. Na_2SO_4 on Strength.

PORTLAND CEMENT.—In general the strength of the portion in the solution was greater than that in air. After two years there was little difference in the bending and compressive strengths of cement B specimens cured in these solutions and those in ordinary water. The other cements were more or less seriously affected. Concrete with cement B took up the least amount of liquid of the

four cements. No simple relation could be obtained between the constitution of the cement and resistance to corrosion.

BLASTFURNACE CEMENT.—The behaviour was similar to that of Portland cement. Cement A was nearly as good as B. The CaO content of A was much lower than that of the other two (V and J).

ALUMINOUS CEMENT.—The corrosion was greatest in the upper portion of the prisms. No strength figures were obtained at two years as the specimens fell to pieces completely.

MIXED CEMENTS.—Trass cement behaves better than Portlandjurament but was not better than Portland cement B. The strength varied from 0.85 to 1.16 that of specimens cured in water.

Effect of 2.4 Per Cent. $MgSO_4$ on Strength.

PORTLAND CEMENT.—Cement B stood up well ; the others were poor.

BLASTFURNACE CEMENT.—Cements A and V were satisfactory. Cement J had a lower compressive strength.

ALUMINOUS CEMENT.—The strength of cement W was very low in parts, while N was satisfactory.

MIXED CEMENTS.—After two years a reduction in strength was clearly noticeable.

Effect of Sea Water on Strength.

PORTLAND CEMENT AND BLASTFURNACE CEMENT.—The strengths were satisfactory.

ALUMINOUS CEMENT.—The strengths of the middle and upper portions were very low or nil.

Effect of 5 Per Cent. NaCl on Strength.

PORTLAND CEMENT AND BLASTFURNACE CEMENT.—No noticeable reduction in strength was observed.

ALUMINOUS CEMENT.—In the middle and upper portions the strength was practically nil.

Effect of Stuttgart Mineral Water on Strength.

All except the mixed cements were satisfactory. The mixed cements had a much lower bending strength, but the compressive strength was not affected.

Effect of Distilled Water and Stuttgart Tap Water on Strength.

Portland and blastfurnace cements stood up well. There was a reduction in strength of the two-year specimens of aluminous cement W.

In general, there was little difference between specimens stored in still and agitated solutions.

The tests show that aluminous cement is not so good as Portland and blastfurnace cements when immersed in Na_2SO_4 solution, $MgSO_4$ solution, sea water, NaCl solution, or mineral water. Aluminous cement specimens stored in closed containers where no evaporation could take place were affected much less than when there was access to the atmosphere.

Tests were made to determine the effect of particle size of the aggregate on corrosion. The grading which gave the most impermeable concrete gave much better results. Concretes with lower cement content were less satisfactory than those with higher.

Cubes Totally Immersed in Solution.

PORTLAND CEMENT.—The results were practically the same as for the prisms.

BLASTFURNACE CEMENT.—The results were practically the same as for the prisms except for the cubes in sea water. In the latter case no corrosion was observed.

ALUMINOUS CEMENT.—The cubes behaved much better than the prisms.

Abstracts from the Foreign Press.

Meta-Alite, a Metastable Form of Alite. By S. Solacolu. *Zement*, No. 40, 1934.—In a series of tests on the behaviour of tricalcium silicate when heated to high temperatures one preparation was found to contain a new substance. This has been shown to be a solid solution of CaO in β-$2CaO.SiO_2$ and has been named meta-alite. Meta-alite was prepared by heating tricalcium silicate to 1,900 deg. C. (its dissociation temperature) and quenching. The product showed no free lime. The X-ray powder diagram was that of β-$2CaO.SiO_2$, but some of the lines had broadened out showing the presence of a solid solution. It appears that the preparation is really in a transition state between tricalcium silicate and the completely dissociated state of a mixture of CaO and $2CaO.SiO_2$. As the formation temperature is 1,900 deg. C. it will not be found in normal Portland cement clinker. It may, however, be present in overburned clinker. Further tests are in hand.

Celite as a Constituent of Portland Cement. By S.Nagai and G. Sawayama. *J. Soc. of Chem. Ind.*, Japan, 1934, p. 581/587.—$4CaO.Al_2O_3.Fe_2O_3$ is formed very easily by heating its constituents at 1,250 deg. C. A mixture of the composition $5CaO:Al_2O_3:Fe_2O_3$ when heated at 1,250 to 1,400 deg. C. contained 5.95 per cent. free lime, further heating at 1,250 to 1,370 deg. C. showed no marked change, but still further heating at 1,400 deg. C. caused the free lime content to rise to 9.05 per cent. At the lower temperature $6CaO.Al_2O_3.2Fe_2O_3$ and $3CaO.Al_2O_3$ are present, which represents 5.14 per cent. free lime. If the mixture is heated directly to 1,400 deg. C. the amount of free lime is 4.9 to 5 per cent. If $3CaO.Al_2O_3$ and $2CaO.Fe_2O_3$ are mixed in equimolecular proportions and heated at 1,320 deg. C. for 40 to 50 hours, 5.3 per cent. free lime is liberated.

Influence of Fineness on the Strength of Portland Cement. By A. Frank. *Zement*, No. 42, 1934.—In the region of 2 to 14 per cent. residue on the 4,900-mesh sieve (approximately 170 meshes per inch) the figures obtained are of definite use. The effect of fineness on the tensile and compressive strength of standard Portland cement mortar made under constant conditions can be expressed by an exponential equation. This equation can be expressed in figures or in a diagram by determining the strengths for two different finenesses. The compressive strength, especially at short dates, is more affected by the fineness than the tensile strength. By finer grinding the ratio of tensile strength to compressive strength is reduced.

Recent Patents Relating to Cement.

Cement Compositions.

412,091. Smitt, G. J. J., Västeras, Sweden. October 27, 1933.

Arsenic is added to cement when cement is being ejected, *e.g.*, from a cement gun, at the place of deposit to cause it to set rapidly with evolution of heat. As_2O_3 is an example given of a compound which may be used in this connection and 2, 3 or 4 parts of this compound with 10 parts of cement and 30 parts of sand are the proportions in which ingredients for the mixture are used.

Cements.

415,985. Soc. des Ciments Francais et des Portland de Boulogne-Sur-Mer et Compagnie des Portland de Desvres, 80, Rue Taitbout, Paris. April 26, 1934.

In the manufacture of white cement the raw materials are mixed with calcium chloride or fluoride or a mixture of the two, the clinker is removed from the hottest zone of the kiln and the clinker immediately cooled either by immersion in water or by steam in a closed vessel screening it from the air. The proportion of chloride or fluoride may range from 2 to 5 per cent. or for a mixture from 2 to 6 per cent.

Cements.

409,166. Soc. Anon. des Ciments Francais et des Portland de Boulogne-Sur-Mer et Compagnie des Portland de Desvres, 80, Rue Taitbout, Paris. July 10, 1933.

Dark cements are prepared from raw materials which are deficient in magnesia by adding to the raw material when it is in the state of powder or slurry magnesia compounds such as dolomite in such amounts as to obtain a clinker which contains from 0.85 per cent. to 2 per cent. magnesia. If desired additional colouring materials such as metallic salts and oxides may be added to increase the colouring effect.

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